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Document Name: APHA Method 4500-S2: Standard Methods for the Examination of Water and Wastewater

CFR Section(s): 40 CFR 136.3(a)

Standards Body: American Public Health Association

Official Incorporator:
THE EXECUTIVE DIRECTOR
OFFICE OF THE FEDERAL REGISTER
WASHINGTON, D.C.

STANDARD METHODS

FOR THE EXAMINATION OF WATER AND WASTEWATER

18TH EDITION 1992

Prepared and published jointly by:

AMERICAN PUBLIC HEALTH ASSOCIATION
AMERICAN WATER WORKS ASSOCIATION
WATER ENVIRONMENT FEDERATION

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1015 Fifteenth Street, NW
Washington, DC 20005

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The Library of Congress has catalogued this work as follows:
American Public Health Association.
Standard methods for the examination of water and wastewater.
ISBN 0-87553-207-1

Printed and bound in the United States of America.
Composition: EPS Group, Inc., Hanover, Maryland
Set in: Times Roman
Printing: Victor Graphics, Inc., Baltimore, Maryland
Binding: American Trade Bindery, Baltimore, Maryland
Cover Design: DR Pollard and Associates, Inc., Arlington, Virginia

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4500-S^{2-} SULFIDE*

4500-S^{2-} A. Introduction

1. Occurrence and Significance

Sulfide often is present in groundwater, especially in hot springs. Its common presence in wastewaters comes partly from the decomposition of organic matter, sometimes from industrial wastes, but mostly from the bacterial reduction of sulfate. Hydrogen sulfide escaping into the air from sulfide-containing wastewater causes odor nuisances. The threshold odor concentration of H_2S in clean water is between 0.025 and 0.25 μg/L. H_2S is very toxic and has claimed the lives of numerous workers in sewers. It attacks metals directly and indirectly has caused serious corrosion of concrete sewers because it is oxidized biologically to H_2SO_4 on the pipe wall.

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* Approved by Standard Methods Committee, 1988.

2. Categories of Sulfides

From an analytical standpoint, three categories of sulfide in water and wastewater are distinguished:

a. Total sulfide includes dissolved H_2S and HS^-, as well as acid-soluble metallic sulfides present in suspended matter. The S^{2-} is negligible, amounting to less than 0.5% of the dissolved sulfide at pH 12, less than 0.05% at pH 11, etc. Copper and silver sulfides are so insoluble that they do not respond in ordinary sulfide determinations; they can be ignored for practical purposes.

b. Dissolved sulfide is that remaining after suspended solids have been removed by flocculation and settling.

c. Un-ionized hydrogen sulfide may be calculated from the concentration of dissolved sulfide, the sample pH, and the practical ionization constant of H_2S.

Figure 4500-S_2^-:1 shows analytical flow paths for sulfide determinations under various conditions and options.

3. Sampling and Storage

Take samples with minimum aeration. To preserve a sample for a total sulfide determination put zinc acetate solution into bottle before filling it with sample. Use 4 drops of 2*N* zinc acetate solution per 100 mL sample. Fill bottle completely and stopper.

4. Qualitative Tests

A qualitative test for sulfide often is useful. It is advisable in the examination of industrial wastes containing interfering substances that may give a false negative result in the methylene blue procedure.

a. Antimony test: To about 200 mL sample, add 0.5 mL saturated solution of potassium antimony tartrate and 0.5 mL 6*N* HCl in excess of phenolphthalein alkalinity.

Yellow antimony sulfide (Sb_2S_3) is discernible at a sulfide concentration of 0.5 mg/L. Comparisons with samples of known sulfide concentration make the technique roughly quantitative. The only known interferences are metallic ions such as lead, which hold the sulfide so firmly that it does not produce Sb_2S_3, and dithionite, which decomposes in acid solution to produce sulfide.

b. Silver-silver sulfide electrode test: The potential of a silver-silver sulfide electrode assembly relative to a reference electrode varies with the activity of the sulfide ion in solution. By correcting for the ion activity coefficient and pH, this potential estimates sulfide concentration. Standardize electrode frequently against a sulfide solution of known strength. An electrode of this type can be used as an end-point indicator for titrating dissolved sulfide with a standard solution of a silver or lead salt, but slow response always is a problem.

c. Lead acetate paper and silver foil tests: Confirm odors attributed to H_2S with lead acetate paper. On exposure to the vapor of a slightly acidified sample, the paper becomes blackened by formation of PbS. A strip of silver foil is more sensitive than lead acetate paper. Clean the silver by dipping in NaCN solution

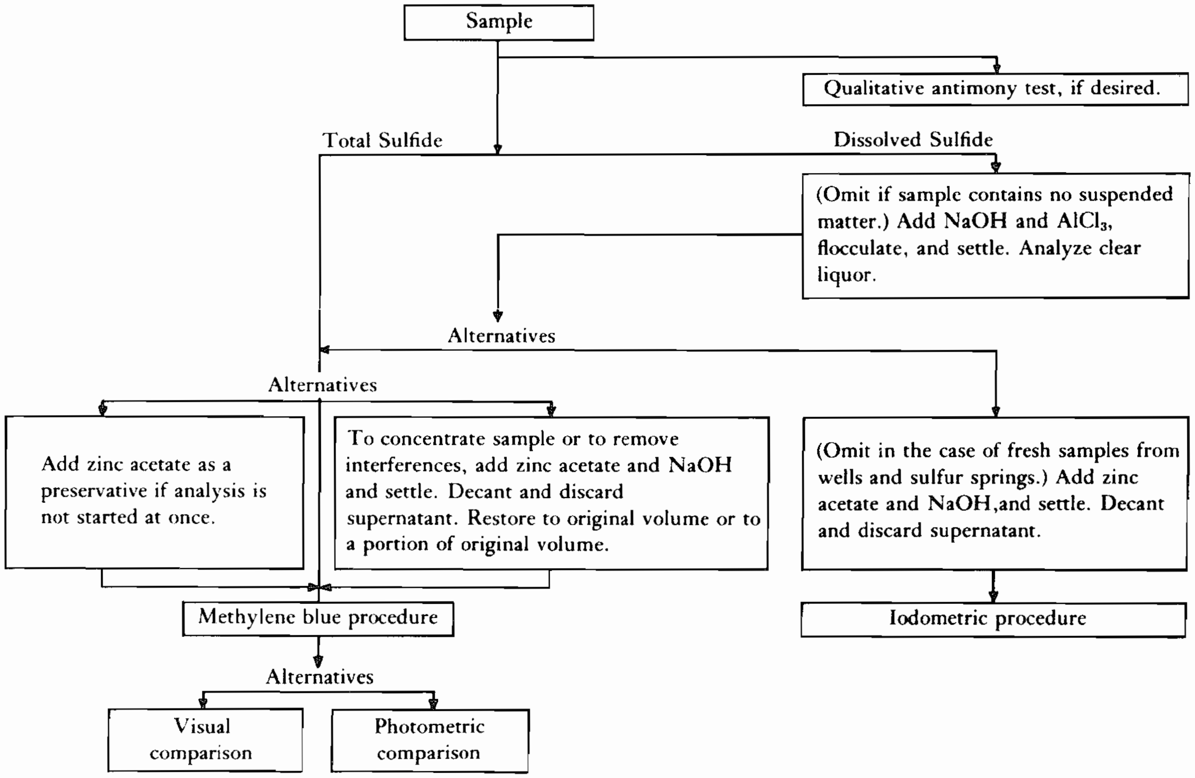
Sample
Qualitative antimony test, if desired.
Total Sulfide
Dissolved Sulfide
(Omit if sample contains no suspended matter.) Add NaOH and AlCl₃, flocculate, and settle. Analyze clear liquor.
Alternatives
Alternatives
Add zinc acetate as a preservative if analysis is not started at once.
To concentrate sample or to remove interferences, add zinc acetate and NaOH and settle. Decant and discard supernatant. Restore to original volume or to a portion of original volume.
(Omit in the case of fresh samples from wells and sulfur springs.) Add zinc acetate and NaOH,and settle. Decant and discard supernatant.
Methylene blue procedure
Iodometric procedure
Alternatives
Visual comparison
Photometric comparison

Figure 4500-S^{2-}:1. Analytical flow paths for sulfide determinations.

4. Procedure

a. Sample collection: Collect a fresh sample taking care to minimize contact with air. Fix cooled samples (<50°C) immediately by adding 1 mL EDTA solution for each 100 mL sample.

b. SO_2 evolution: Prepare the absorbing solution by adding 5 mL 1,10-phenanthroline solution, 0.5 mL ferric ammonium sulfate solution, 25 mL distilled water, and 5 drops octyl alcohol (to act as defoamer) to a 100-mL nessler tube; insert a gas dispersion tube. Add 1 mL sulfamic acid solution to the gas washing bottle and 100 mL of sample or a portion containing less than 100 μg SO_3^{2-} diluted to 100 mL. Add 10 mL 1 + 1 HCl and immediately connect the gas washing bottle to the gas train as shown in Figure 4500-SO_3^{2-}:1. Place a spring or rubber band on the gas washing bottle to keep the top securely closed during gas flow. Adjust nitrogen flow to 2.0 L/min and purge for 60 min.

c. Colorimetric measurement: After exactly 60 min, turn off nitrogen flow, disconnect nessler tube, and immediately add 1 mL ammonium bifluoride solution. Remove gas dispersion tube after rinsing it with distilled water into the tube and forcing the rinse water into the nessler tube with a rubber bulb. Dilute to 50 mL in the nessler tube and mix by rapidly moving the tube in a circular motion. Do not let rubber stoppers or PVC tubing come in contact with the absorbing solution. After at least 5 min from the time of adding ammonium bifluoride, read the absorbance versus distilled water at 510 nm using either a 5-cm cell for a range of 0 to 30 μg SO_3^{2-} per portion or a 1-cm cell for a range of 0 to 100 μg SO_3^{2-}. Avoid transferring octyl alcohol into the cell by letting it rise to the surface of the absorbing solution and transferring the clear lower solution to the cell with a pipet. Make a calibration curve by analyzing a procedure blank and at least three standards. Run at least one standard with each set of samples. For maximum accuracy hold samples and standards at the same temperature and keep the time interval from start of purging to the addition of ammonium bifluoride constant. This is easier to do if several gas trains are used simultaneously in parallel. If ambient temperatures are subject to frequent fluctuation, a water bath may be used to control color development at a fixed temperature.

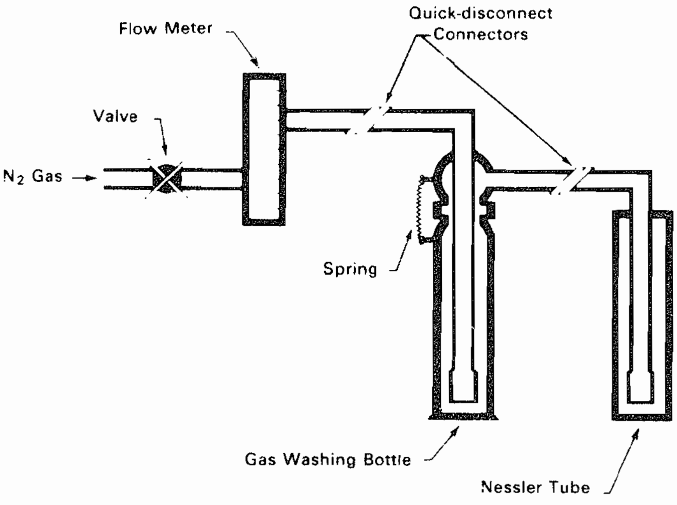

Figure 4500-SO_3^{2-}:1. Apparatus for evolution of SO_2 from samples for colorimetric analysis.

5. Calculation

$$\text{mg } SO_3^{2-}/\text{L} = \frac{\mu\text{g } SO_3^{2-} \text{ from calibration curve}}{\text{mL sample}}$$

6. Precision and Bias

Three laboratories analyzed five replicate portions of a standard sulfite solution and of secondary treated wastewater effluent to which sulfite was added. The data are summarized below. Individual analyst's precision ranged from 4.1 to 10.5% standard deviation (*N* = 45).

Sample	$\bar{X}$ *mg/L*	Standard Deviation, σ *mg/L*	Relative Standard Deviation %
Standard, 4.7 mg SO_3^{2-}/L	3.7	0.78	21
Secondary effluent with 0.12 mg SO_3^{2-}/L	0.12	0.03	25
Secondary effluent with 4.0 mg SO_3^{2-}/L	3.7	0.30	8. 0

7. References

1. STEPHENS, B.G. & F. LINDSTROM. 1964. Spectrophotometric determination of sulfur dioxide suitable for atmospheric analysis. *Anal. Chem.* 36:1308.
2. WEST, P. W. & G.C. GAEKE. 1956. Fixation of sulfur dioxide as sulfitomercurate and subsequent colorimetric determination. *Anal. Chem.* 28:1816.

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